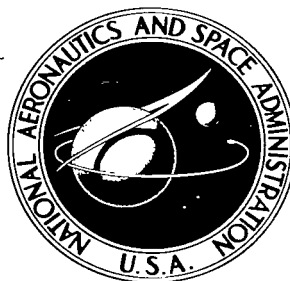


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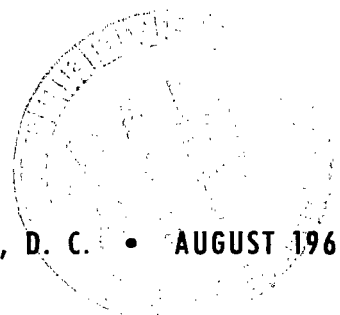
THE X-IRRADIATION OF HYDRAZINE AND 1,1-DIMETHYLHYDRAZINE

by Harold Lucien and Murray L. Pinns

Lewis Research Center

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • AUGUST 1964





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SUMMARY

Hydrazine and 1,1-dimethylhydrazine were radiolyzed at room temperature by using about 1 gram of liquid or 1/2 to 2 liters of vapor at room-temperature vapor pressure. A tungsten-target X-ray source operating at 300 kilovolts and 6 to 8 milliamperes (0.1 to 1.0 A) was used at intensities of 1×10^2 to 1×10^3 roentgens per minute to give total doses of 4.1 rads to 2.3×10^6 rads. The amounts of decomposition were dependent on total dose and independent of dose rate. In the case of hydrazine vapor, the decomposition was also directly related to surface area. There was a lesser surface effect with liquid hydrazine, but this variable was not studied for 1,1-dimethylhydrazine. The order of decreasing sensitivity to X-radiation is as follows: hydrazine vapor, 1,1-dimethylhydrazine vapor, 1,1-dimethylhydrazine liquid, and hydrazine liquid. The decomposition products of hydrazine were nitrogen, hydrogen, ammonia, and unidentified products. The same products plus methylamine, dimethylamine, and hydrazine were found from the decomposition of 1,1-dimethylhydrazine. In addition, the 1,1-dimethylhydrazine underwent postirradiation changes. Values for G (number of molecules of sample decomposed per 100 ev of absorbed energy) of the order of 10^6 suggest that the vapor-phase decompositions are chain reactions.

INTRODUCTION

This study is a continuation (ref. 1) of an effort to determine the effects of ionizing radiation on the space storability of chemical rocket propellants. The total dose of X-rays used is representative of that expected through 0.015 inch of stainless steel over a period of about 2 years at 0.6 to 1.0 astronomical units from a quiet sun (refs. 2 and 3).

The investigation was limited to a survey of the effects of X-rays (0.1 to 1.0 A) on liquid and vapor samples of hydrazine and 1,1-dimethylhydrazine (UDMH) in borosilicate glassware at room temperature and at intensities of 1.0×10^2 to 1.0×10^3 roentgens per minute. Dose-damage relations were determined for the radiation decomposition of the two phases of both compounds. Information was also obtained concerning the dependence of the hydrazine-vapor decomposition on surface area.

APPARATUS AND PROCEDURE

Starting materials were 99.9-percent pure and were obtained from commercial products by dehydration over calcium hydride and low temperature bulb-to-bulb fractionation as described in reference 4. Freshly distilled products were used for each radiation experiment. Irradiations were conducted in sealed borosilicate glassware. Gas cells (fig. 1(a)) were spherical and of 1- or 2-liter capacity; liquid cells (fig. 1(b)) were constructed from 8-millimeter-inside-diameter glass tubing and had capacities of approximately 10 milliliters. Both liquid and gas cells were provided with side arms to permit the introduction of the sample and the transference of irradiation products from the cell to the vacuum system. In addition, gas cells were provided with a pressure transducer to follow pressure changes during the irradiation and a U-shaped trap for condensing the contents of the cell.

The glassware was cleaned with a sulfuric-nitric acid mixture, rinsed with tap and distilled water, and oven dried. Irradiation cells were degassed at 10^{-6} millimeter of mercury and 300°C and charged with a known quantity of sample. Liquid nitrogen was used to freeze the sample while the cell was sealed off and removed from the vacuum line. The liquid cell was placed in a bored lead brick that contained a port on the front face that was continuous with the bore (fig. 1(b)). In this manner, approximately half of the liquid was exposed to primary X-radiation. The entire gas cell was exposed to the beam while a $1/2$ -inch lead shield protected the pressure transducer. Borosilicate-glass tubing (1.72-mm O.D., 20-mm length, and 0.2-mm wall) was inserted into the gas cell to provide additional surface as was required.

The X-radiation was provided by a tungsten-target generator operating at 300 kilovolts and 6 to 8 milliamperes. Intensities in the range 1×10^2 to 1×10^3 roentgens per minute were used.

In order to confirm that the radiation intensity was constant, the dose rate was monitored continuously with a roentgen rate meter which was equipped

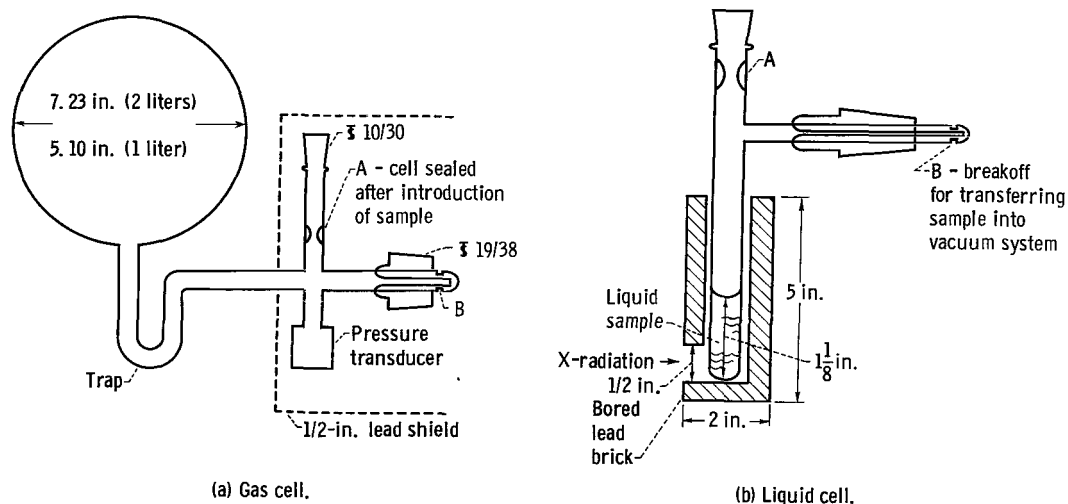


Figure 1. - Borosilicate cells used to irradiate hydrazine and 1, 1-dimethylhydrazine.

with a probe that was covered with a borosilicate-glass thimble of the same thickness as the irradiation cell wall. This probe was placed next to the liquid samples and at the spherical surface nearest the X-ray port for gas samples. The absorbed radiation dose was determined by first conducting ferrous sulfate dosimetry in cells having the same dimensions as the radiation cells ($\text{Fe}^{+2} \rightarrow \text{Fe}^{+3}$, $G = 15.5 \pm 0.4$ where G is the number of ferrous ions converted to ferric ions per 100 ev of absorbed energy) by the method of reference 5 and then by multiplying the result by the ratio of the electron density of the irradiated compound to the electron density of the ferrous sulfate solution.

An indication of the rates of degradation in the vapor-phase irradiations was obtained from the pressure-time traces; however, most of the data were obtained from chemical analyses performed within 1/2 hour after absorption of the predetermined doses. Liquid samples were first frozen in liquid nitrogen, and the permanent gases, nitrogen and hydrogen, were pumped off and analyzed by gas chromatography and mass spectroscopy. These samples were then roughly fractionated by being passed through a series of traps maintained at different reduced temperatures. The contents of each trap were analyzed by infrared spectroscopy or gas chromatography. Retained samples of many of the fractions were sealed off in glass ampoules and stored at room temperature. The irradiated vapor samples were first frozen in liquid nitrogen and the permanent gases were

TABLE I. - X-IRRADIATION OF HYDRAZINE^a

Experiment	Sample weight, g	Dose rate (meter) r/min	Dose rate (ferrous sulfate solution) r/min	Irradiation time, hr	Dose absorbed by sample, rads	N ₂ H ₄ decomposed, percent	Volume N ₂ +H ₂ formed (STP) ^b , ml	Ratio of nitrogen to hydrogen, N ₂ /H ₂	Values of G for decomposition of hydrazine	Sample volume, cu cm	Cell surface area, sq cm
Liquid											
1	0.900	1.0x10 ³	1.0x10 ³	41.7	2.4x10 ⁶	1.6	1.7	1.5	2.0x10 ²	----	7.7
2	.900	1.0	1.0	25.0	1.4	1.0	.2	1.0	2.1	----	7.7
3	.898	1.0	1.0	25.0	1.4	2.0	.3	.5	4.2	----	26.6
4	.907	.5	.5	33.3	.95	.8	.2	1.0	2.5	----	7.7
5	.905	1.0	1.0	16.7	.95	.9	---	1.0	2.9	----	7.7
Vapor											
6	0.025	1.0x10 ³	0.38x10 ³	25.0	13	2.9	9.1	2.0	6.6x10 ⁷	1020	530
7	.047	1.0	.48	25.0	16	1.8	3.2	2.0	3.5	2050	780
8	.025	1.0	.38	25.0	13	30.6	14.7	.5	70	1020	1890
9	.025	1.0	.38	25.0	13	14.9	10.3	.5	34	1020	1330
10	.025	1.0	.38	41.7	22	4.5	5.7	2.0	6.2	1020	530
11	.015	.1	.084	81.7	12	3.0	---	2.0	7.8	500	300
12	.024	.1	.038	250	13	3.0	---	2.0	7.1	1020	530

^a All irradiations conducted at room temperature, approximately 28° C.

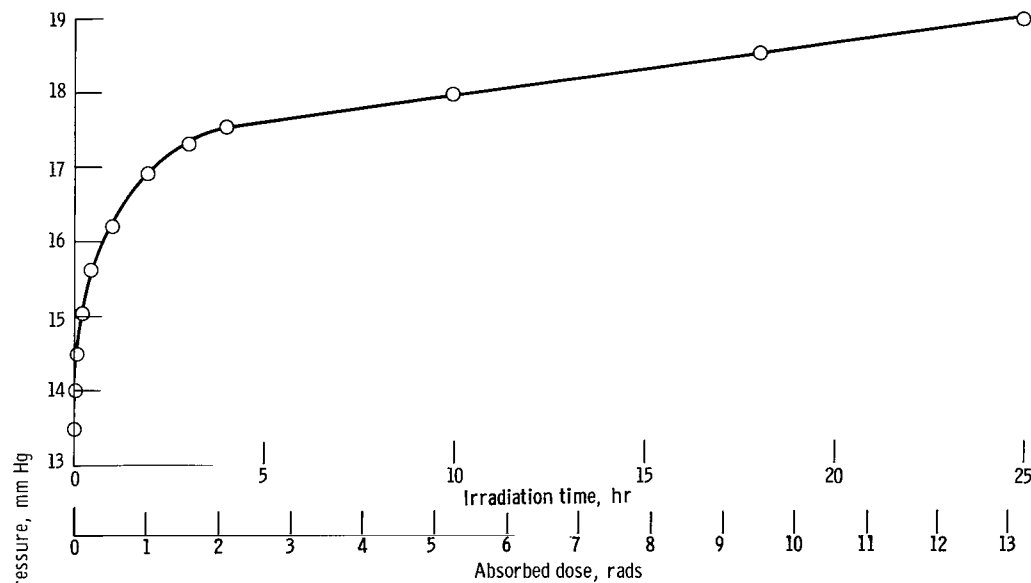
Vapor irradiations conducted under an initial pressure of approximately 13.5 mm Hg, vapor pressure of hydrazine at room temperature.

^b Standard temperature and pressure.

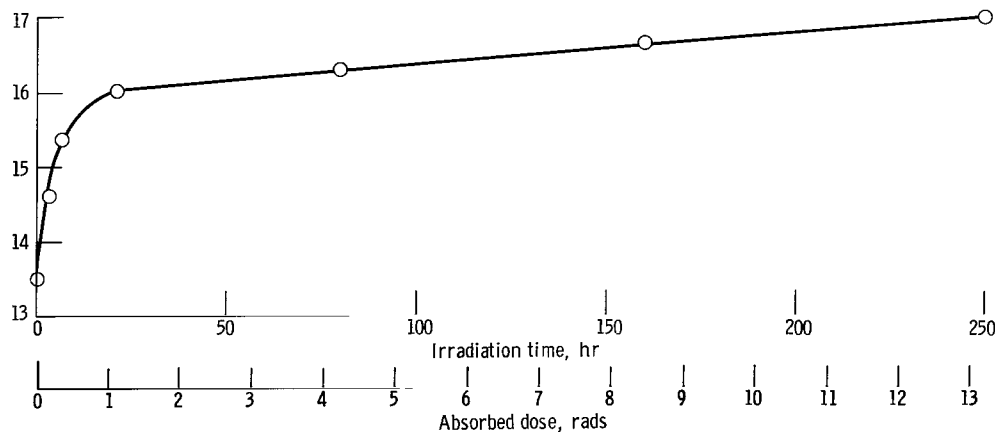
pumped off. They were then analyzed by infrared spectroscopy without further fractionation.

RESULTS AND DISCUSSION

Data from the X-irradiation of hydrazine and 1,1-dimethylhydrazine are summarized in tables I and II. These and other results are considered in the following sections.



(a) Experiment 8; dose rate, 1000 roentgens per minute; cell surface area, 1890 square centimeters.



(b) Experiment 12; dose rate, 100 roentgens per minute; cell surface area, 530 square centimeters.

Figure 2. - X-irradiation of hydrazine vapor. Sample size, 0.025 gram.

X-Irradiation of Hydrazine

Typical results for the X-irradiation of hydrazine are given in table I. The effect of dose rate is considered first. Two 0.025-gram samples of vapor (experiments 6 and 12) were irradiated at 380 and 38 roentgens per minute, respectively, to a total dose absorption of 13 rads, and a similar extent of decomposition (~ 3 percent) was observed for both samples. The G values and the ratios of nitrogen to hydrogen were also the same for the two runs. Similarly, two 0.9-gram liquid samples (experiments 4 and 5) were exposed to 0.5×10^3 and 1.0×10^3 roentgens per minute, respectively, to total dose absorptions of 9.5×10^5 rads for which about 0.9-percent decomposition was observed. Again the G values and ratios of nitrogen to hydrogen were the same. Therefore, over the range of X-ray doses absorbed, the radiation dose rate does not affect the net decomposition for the same total absorbed dose, all other conditions remaining constant.

A plot (fig. 2) of pressure against absorbed dose shows that there is an initial nonlinear period in the decomposition of hydrazine vapor; however, this initiation period of about 2 to 4 hours is relatively short compared to the total irradiation times in excess of 25 hours. After the initiation process, the pressure, and therefore presumably the percent decomposition, of the vapor increased linearly with absorbed dose. As shown in figure 3(a), the percent decomposition of liquid hydrazine also increased proportionally to the total dose. The change in decomposition of hydrazine vapor with dose is shown in figure 3(b).

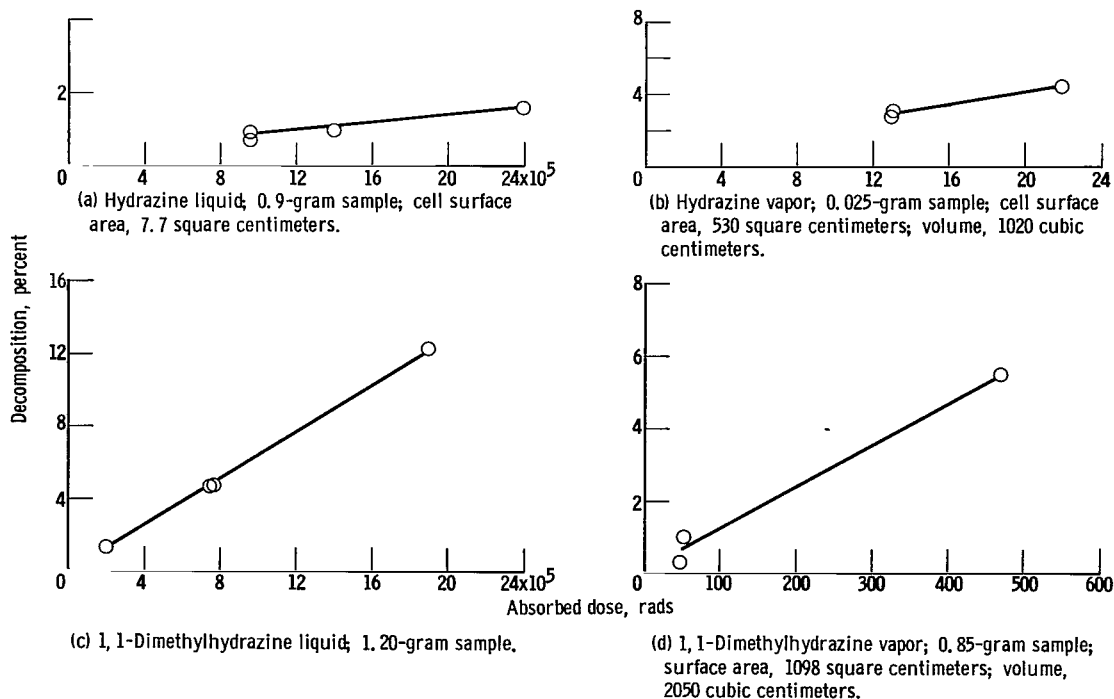


Figure 3. - Effect of size of absorbed X-ray dose on percent decomposition of hydrazine and 1,1-dimethylhydrazine (UDMH).

In the hydrazine experiments the absorbed dose was about 10^5 times greater in the liquid than in the vapor phase for approximately the same intensity and time of exposure. The calculated G values show that the decomposition per rad absorbed was about 10^5 times greater in the vapor phase, depending on the surface area and the pressure of the vapor.

Some of the work done was aimed at determining the effects of surface on the decomposition of hydrazine. This work was somewhat complicated because glass is activated by X-radiation, and the rate of decomposition is higher in irradiated glassware than in new glassware. Borosilicate glass turns dark brown under X-rays and, while part of this color bleaches out after exposure, most of the tint is permanent and can only be removed by fusing the glassware. Active sites on the surface of the tinted glass may play an important role in sustaining chemical reactions. In any case, reproducible results could only be obtained after the glass was irradiated by 2×10^6 roentgens, and the data reported herein were obtained after such treatment.

The effect of surface on the vapor-phase decomposition is shown in experiments 6 through 12 of table I and is plotted in figure 4. Experiments 6, 8,

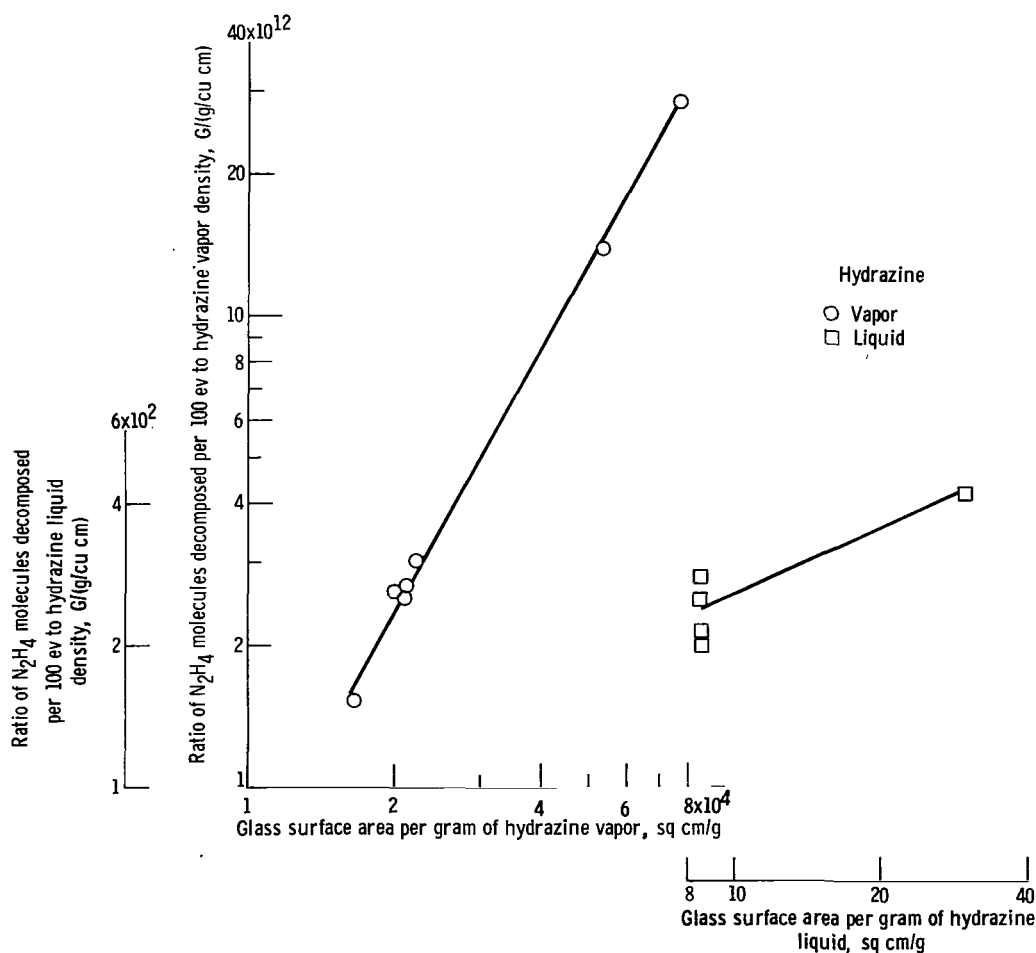


Figure 4. - Effect of surface area on hydrazine decomposition.

and 9, were identical except that in the last two experiments the cell was packed with capillary borosilicate-glass tubing to increase the surface area. In the other experiments, cells of larger and smaller volume were used, and the sample size, the absorbed dose, and the dose rate were different. Figure 4 shows that the results fit an equation of the form

$$G = C\rho\left(\frac{S}{m}\right)^n$$

where

G number of molecules of sample decomposed per 100 electron volts of absorbed energy

ρ density, g/cu cm

S glass surface, sq cm

m sample weight, g

n, C constants

For hydrazine vapor, the exponent n is approximately 1.9. The data for liquid hydrazine are much more limited, but when also plotted in figure 4, indicate a much smaller exponent, approximately 0.6. Once reaction started, the surfaces were covered with small bubbles. It might be expected that a much higher rate would then be observed since the reaction rate would be higher in the gas phase than in the liquid phase. Possibly active intermediates are quenched in the liquid phase.

The irradiation of hydrazine (N_2H_4) formed, in addition to nitrogen, hydrogen, and ammonia, small amounts of materials having higher molecular weights than hydrazine, as was shown by gas chromatography. These materials were unstable and were best observed by freezing out the radiation products in liquid nitrogen prior to turning off the X-rays.

X-Irradiation of 1,1-Dimethylhydrazine

Data for the liquid- and vapor-phase irradiations of UDMH are given in table II. All vapor-phase experiments were performed in X-ray aged, 2-liter flasks. The effect of varying surface area was not studied. The percent liquid decomposed was again proportional to the absorbed dose (fig. 3(c)). The effect of the dose on vapor decomposition is shown in figure 3(d).

As with N_2H_4 , the decomposition of UDMH per rad absorbed is several orders of magnitude higher in the vapor than in the liquid phase. A pressure-dose plot for the vapor-phase reaction is shown in figure 5. The initial reduction in pressure indicates that a polymerization reaction and possibly some condensation occurs in the early stages of the X-irradiation. This initial reduction is followed by a relatively rapid increase in pressure and then by a slower

TABLE II. - X-IRRADIATION OF 1,1-DIMETHYLHYDRAZINE (UDMH)^a

Experiment	Sample weight, g	Dose rate (meter) r/min	Dose rate (ferrous sulfate solution) r/min	Irradiation time, hr	Dose absorbed by sample, rads	UDMH decomposed, percent	Volume N ₂ +H ₂ formed (STP) ^b , ml	Ratio of nitrogen to hydrogen, N ₂ /H ₂	Values of G for decomposition of UDMH
Liquid									
13	5.96	0.86×10 ³	0.86×10 ³	14.7	5.7×10 ⁵	3.40	0.5	0.5 ↓	9.6×10 ²
14	1.20	.86	.86	19.6	7.5	4.70	1.0		10
15	1.20	1.0	1.0	41.7	19	12.3	2.5		11
16	1.20	1.0	1.0	4.17	1.9	1.31	.3		11
17	1.20	.5	.5	33.3	7.5	4.69	1.1		10
Vapor									
18	0.85	0.94×10 ³	0.48×10 ³	4.5	51	1.0	0.5	1.5	3.1×10 ⁶
19	.85	1.0	.48	41.7	470	5.5	.8	2.0	1.9
20	.86	1.0	.48	4.17	48	.3	.3	.5	1.0

^aAll irradiations conducted at room temperature, approximately 28° C.

Vapor irradiations conducted in 2050 cu cm cell under approximately 145 mm Hg, vapor pressure of 1,1-dimethylhydrazine at room temperature.

^bStandard temperature and pressure.

steady pressure increase. Unstable compounds were found in samples taken during the time of minimum pressure. These compounds decomposed in 5 to 20 minutes at room temperature to hydrogen, nitrogen, dimethylamine, and traces of other components.

All the irradiated UDMH samples produced ammonia, dimethylamine, nitrogen, hydrogen, and other products. When the product from experiment 13 (table II) was separated into seven fractions by a two-stage trap-to-trap fractionation, it was found to contain hydrogen, nitrogen, ammonia, methylamine, dimethylamine, undecomposed UDMH, and three probably different, unstable components. The fractions containing these unstable components decomposed in about 2 months at room temperature to form, in part, additional amounts of hydrogen, nitrogen, ammonia, and dimethylamine, and, in part, small quantities of viscous liquids with very low vapor pressures. The latter liquids were not volatile at 10⁻⁶ millimeters of mercury and room temperature. One of these residues was dark

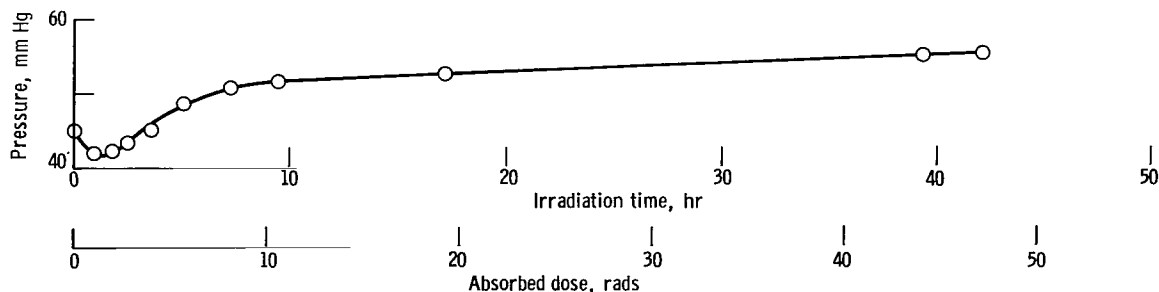


Figure 5. - The X-irradiation of 1,1-dimethylhydrazine vapor. Sample weight, 0.9 gram; dose rate, 1000 rads per minute.

blue initially, turned red on pumping, but reverted to dark blue on standing; another residue was brownish red.

A significant aspect of the irradiation of hydrazine and UDMH is the possibility of postirradiation reactions induced by the primary radiation effect. The phenomenon of postirradiation change was most pronounced with UDMH vapor. Similar effects, though small, were observed with the liquids. Formation of viscous products of the kind described was not observed with hydrazine, although transient products of molecular weights greater than hydrazine were suspected.

SUMMARY OF RESULTS

Hydrazine and 1,1-dimethylhydrazine (UDMH) liquid and vapor (the vapors at approximately 13.5 and 145 mm of Hg abs, respectively) were subjected to 0.1- to 1.0-Angstrom X-rays at room temperature and at a dose rate of 100 to 1000 roentgens per minute. The total absorbed doses ranged from 4.1 rads to 2.3×10^6 rads. The following results were obtained:

1. Decompositions ranged from 0.3 to 31 percent. The order of decreasing sensitivity to X-rays was as follows: hydrazine vapor, UDMH vapor, UDMH liquid, and hydrazine liquid.

2. The primary radiolysis products from hydrazine were nitrogen, hydrogen, ammonia, and traces of unidentified products. The products from UDMH were nitrogen, hydrogen, ammonia, hydrazine, methylamine, dimethylamine, and unidentified products.

3. Values for G (number of molecules of sample decomposed per 100 ev absorbed) were very high, of the order of 10^6 to 10^8 , for the vapor-phase irradiations. For the liquid irradiations they were of the order of 10^2 to 10^3 .

4. The G value for the decomposition of hydrazine vapor was directly proportional to the first power of the vapor density and the 1.9 power of the glass surface per weight of vapor. For liquid hydrazine, the surface area per unit weight entered only as approximately the 0.6 power.

5. The extent of decomposition was directly related to the total dose of radiation for the liquids and probably also for the vapors. It appeared to be independent of the dose rate.

6. Irradiated UDMH liquid and vapor underwent postirradiation change, and unknown viscous products were formed. The effect was most pronounced with UDMH. Hydrazine did not show this behavior.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, June 22, 1964

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